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AN IMPROVED VICTOR-MEYER MOLECULAR-WEIGHT APPARATUS [1]

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ABSTRACT

The Victor-Meyer molecular-weight apparatus for determining vapor density is modified to permit measurements at two pressures, one atmosphere and one-half atmosphere. By using Berthelot's method of limiting density most of the effects of departure from the perfect gas laws are eliminated. Experiments with hydrocarbons gave molecular weights differing from the theoretical by the following maximum deviations: Benzene, 16 experiments, 0.2 per cent; hexane, 4 experiments, 0.24 per cent; naphthalene, 4 experiments, 0.06 per cent.

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I. INTRODUCTION

The Victor-Meyer method for molecular-weight determinations in the vapor state, as ordinarily carried out, involves the assumption that the vapor obeys the Boyle and Avogadro laws at the temperature of the experiment. Since this temperature is seldom very much above the normal boiling point of the substance, the departure from the gas laws is by no means inconsiderable.

MacInnes and Kreiling [2] have shown that this source of error can be removed by calculating the molecular weight from the Berthelot equation and the critical-point constants of the substance and that when this is done the accuracy of the method is very materially improved.

For practical purposes, however, this procedure suffers from the disadvantage that in no actual case will the critical-point data be known, if the molecular weight is unknown. The obvious method of removing this difficulty is to make use of Berthelot's method of limiting density by carrying out the measurements at two pressures. This paper describes an apparatus and technic by means of which this can be conveniently accomplished.

[1] This study was undertaken in connection with an investigation on "The Separation, Identification and Determination of the Chemical Constituents of Commercial Petroleum Fractions" listed as project No. 6 of the American Petroleum Institute research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the institute with the cooperation of the Central Petroleum Committee of the National Research Council.

[2] MacInnes and Kreiling, J. Am. Chem. Soc., 39, p. 2350; 1917.

II. APPARATUS AND PROCEDURE

A method for using reduced pressure in determining the vapor density of substances which have high boiling points and which may decompose at high temperatures, has been developed by Lunge and Neuberg.[3] Their procedure was to measure the volume of air displaced by a definite mass vaporized at a known temperature and pressure. No application of this work to the determination of molecular weights was made at this time. However, later applications have been made, notably by Ramsay and Steele,[4] whose work will be discussed later in this paper.

In the present work, the objective is to determine molecular weights, both accurately and rapidly, and without the use of the critical data. For this purpose two complete measurements are necessary. One is made at one atmosphere and the other at one-half atmosphere. The apparatus used is a modification of the Victor-Meyer type. It was designed to gain compactness of form, thus avoiding the well-known difficulties of local temperature differences which result from undue length of the vaporizing chamber.

However, a short vaporizing chamber greatly increases the possibility of errors resulting from diffusion of the vapor, which may condense in the adjoining burette. Diffusion is particularly liable to occur when the experiment is being carried out under reduced pressure. This possibility has been practically eliminated in the vaporizing unit shown in Figure 1.

The vaporizing chamber is about 40 cm in length, about 7 cm outside diameter, and has a capacity of approximately 1 liter. It is made of heavy-walled pyrex glass. It consists of an inner tube, *E*, of 10 mm outside diameter, surrounded by a series of bulbs of consecutively diminishing volume, *J* to *G*. The connections between the bulbs are tubes 11 mm in diameter, which provide a narrow gas passage between the bulbs. A quick, jerky displacement of the air, which may result from the sudden release of the vapor in a single or unrestricted vaporizing space, is thus avoided. The volume of the vapor formed by the sample is considerably less than the volume of bulb *J*. If a portion of the vapor should diffuse out of this bulb, it would obviously be greatly diluted in the succeeding bulb, and the effluent air from *G* should be free from the vapor.

The tube inclosed by the vaporizing chamber ends about 3 cm above the bottom of bulb *J*. It projects through a ring seal at the top of *G*, and is flared with a shoulder *C*. It has an enlarged opening, which is fitted with a ground glass stopper *B* for convenience in introducing the bulb containing the sample.

Two tungsten wire leads (diameter about 1 mm) are sealed through the stopper *B*. These are accessory to the breaking apparatus. Two designs of breaking apparatus have been employed. They are shown in details 1 and 2 of Figure 2. Both are made of brass and will fit closely (allowing for expansion) into the inner tube *E*. Unit 1 is fitted into a cork ring, which rests on the shoulder, *C*, and is used with the stopper *B*. It extends about 2.5 cm below tube, *E*, and is perforated with 3 mm openings. The sample bulb is introduced through

[3] Lunge and Neuberg, Ber., **24**, p. 729; 1891.
[4] Ramsay and Steele, Z. phys. Chem., **44**, p. 348; 1903.

a threaded plug at the bottom. The plunger, *H*, rests on the bulb. A steel weight, *D*, is suspended by a silk thread from a 0.5 ampere fuse wire across the tungsten leads *A*. A small electrical current is passed through these leads in order to melt the fuse wire and release the weight, *D*. The impact of *D* on the plunger, *H*, shatters the capillary tip of the bulb and allows the vapor to escape.

The alternate design 2 is used without the ground-glass stopper *B*. It is inserted through a cork stopper, which is fitted under flange *V*. It is then placed in the opening, *C*, and sealed with deKhotinsky cement. The plunger, *H*, is controlled by a rod at the upper end, threaded which passes through the fixed nut *P* and the double flange *V*. The flange is made vapor tight by a special packing of asbestos fiber and graphite. The plunger is operated by turning *T*.

The sample bulb is made from pyrex glass tubing 4 mm in diameter and of calculated length. Each end is drawn down to a small capillary tube. A fine scratch is made about 8 mm from the end of each capillary. The bulb is weighed and then filled with the substance. To accomplish this, one of the capillary ends is immersed in the substance (in liquid form) and slight suction applied to the other end. The bulb must have sufficient strength and contain enough vapor space to withstand the pressure from expansion of the sample when it is brought to equilibrium temperature within the vaporizing chamber. Before sealing the ends of the bulb, the air remaining in the space left for expansion is displaced by vapor from the gently heated substance. The capillary ends are then sealed in the tip of an oxy-gas flame. The bulb is weighed again and the weight of the sample is obtained by difference. The bulb is then placed in the breaking apparatus, which, in turn, is adjusted to position in the vaporizing chamber.

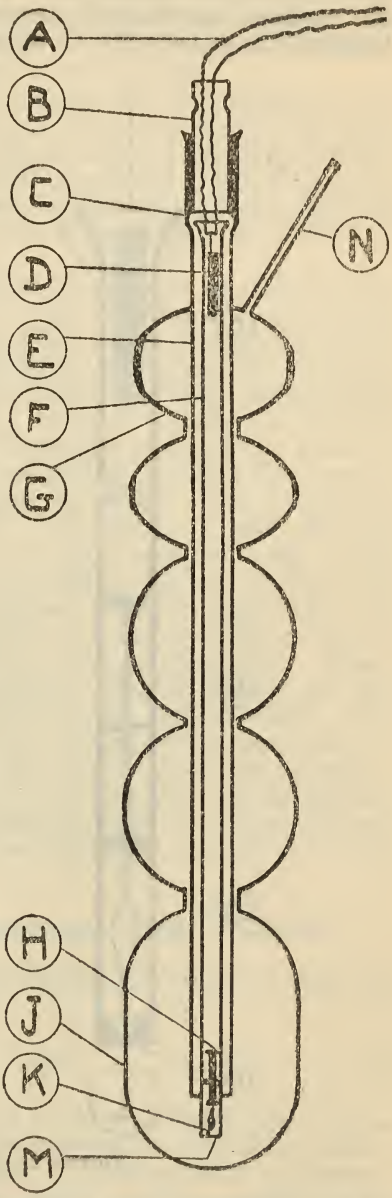

FIGURE 1.—*The vaporizing unit with breaking apparatus*

(1) Shown in position.

The vaporizing chamber is surrounded by an oil bath, which is kept within 0.05° C. of the proper operating temperature by an inclosed mercury-in-glass thermostat. Uniformity of temperature is insured by vigorous mechanical stirring. The bath is maintained at a temperature at least 50° C. above the boiling point of the substance

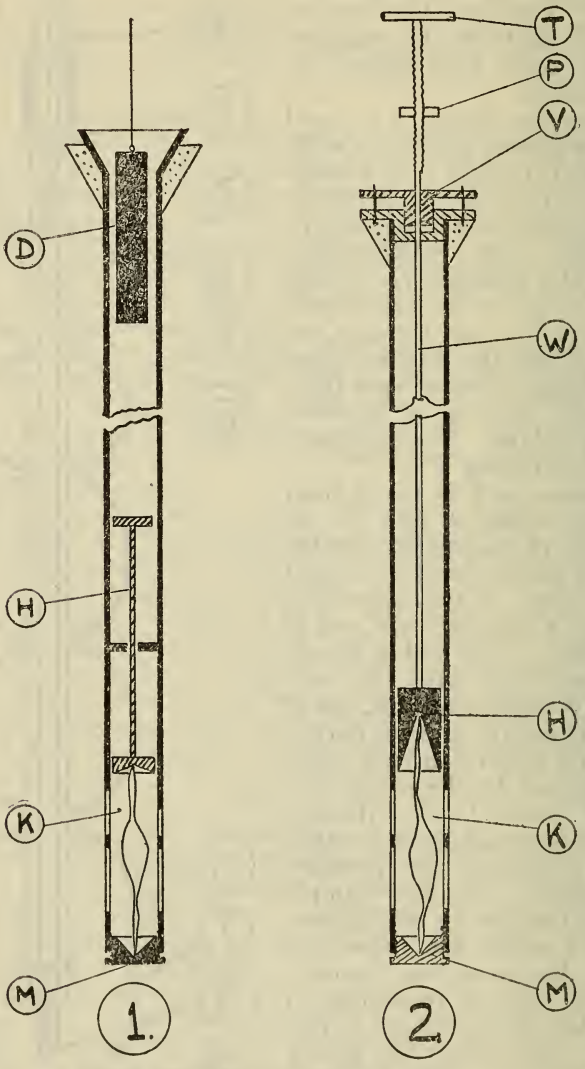

FIGURE 2.—*The breaking units*

to be vaporized. The constancy of the temperature control may be checked by treating the apparatus as a constant pressure gas thermometer.

The volume of the vaporized sample is obtained by measuring, at room temperature and a known pressure, the volume of air which it displaces. The technic and assembly of the manometric apparatus

employed are identical with those used by this bureau[5] in gas analysis, with the exception that the manometer is made longer and provided with an additional platinum contact to facilitate measurements at 0.5 atmosphere. Provision is also made for partial evacuation of the apparatus and for filling it with nitrogen instead of air in cases where cracking or oxidation of the substance is to be feared.

The capillary outlet from the vaporizing unit is adapted to the connecting tube of the measuring system by means of a ground-glass joint sealed with a lubricant which will withstand high temperatures. A flexible glass coil, of thin walled, soft glass tubing about 2 mm in diameter, is placed between the joint and the manometer stopcock. This expansion coil permits connecting the rigidly fixed burette to the vaporizing unit.

The technic employed in a complete operation is as follows: The sample bulb, which has been placed in the apparatus as previously described, is allowed to remain in position until temperature equilibrium (about two minutes) is established throughout the chamber. During the interval of time allowed for this to take place, adjustments are made in the measuring system to establish equality of pressure throughout. When equilibrium has been attained and the pressure balance established, the barometric reading is recorded (for atmospheric pressure) and the compensator is closed. The bulb containing the sample is then crushed. The stopcocks and leveling bulb of the burette are adjusted to allow the mercury level to fall slowly, and the air displaced by the vaporized substance to flow over into the burette. Care is taken to prevent a sudden rush of air and resulting inequalities of pressure which may cause diffusion of the vapor and consequent errors resulting from condensation. When there is no further displacement apparent, time is allowed for the temperature equilibrium in the burette to be reestablished. The pressure is again adjusted to the known pressure of the compensator. The volume and temperature of the air in the burette are recorded.

For the measurement made at the lower pressure, the above procedure is repeated except that the pressure balances are established at 0.5 atmospheres by partially evacuating the apparatus at the beginning of the determination.

III. CALCULATION OF THE MOLECULAR WEIGHT

The Berthelot equation for limiting density, rearranged to give the molecular weight, is as follows:

$$M=\frac{mRT}{pv}(1+Ap) \qquad (1)$$

where M is the molecular weight, R is the gas constant, and A is a coefficient which represents the deviation from the perfect gas laws. The experimental values for m (mass), T (temperature in degrees absolute), p (pressure in atmospheres), and v (volume) are first substituted from the data obtained in the series of observations at ap-

[5] Shepherd, B. S. Jour. Research, 4, p. 3; 1930.

proximately one atmosphere and in the series at approximately 0.5 atmosphere pressure and the resulting equations added together thus:

$$M_1+M_2+M_3+\text{----}M_n=\frac{D_1RT_1}{P_1}(1+Ap_1)+\frac{D_2RT_2}{p_2}(1+Ap_2)$$
$$+\frac{D_3RT_3}{p_3}(1+Ap_3)+\text{------}\frac{D_nRT_n}{p_n}(1+Ap_n)=R\frac{D_1T_1}{p_1}$$
$$+\frac{D_2T_2}{p_2}+\frac{D_3T_3}{p_3}+\text{------}\frac{D_nT_n}{p_n}+A\ (D_1T_1+D_2T_2+D_3T_3$$
$$+\text{------}D_nT_n)$$

which has the form:

$$M=R(C_1+C_2A)$$

Likewise the equations for 0.5 atmosphere may be reduced to:

$$M=R(C'_1+C'_2A)$$

or

$$C_2A-C'_2A=C'_1-C_1$$

and

$$A=\frac{C'_1-C_1}{C_2-C'_2} \tag{2}$$

The value of A so calculated is now substituted in equation (1) and the molecular weight is calculated for each determination.

In the above calculation it is assumed that the vapor density is a linear function of the pressure, or rather, that the straight line through the plotted determinations at one and at one-half atmosphere passes through the correct value of the limiting density for zero pressure. This is not strictly true. The magnitude of the discrepancy is, however, small as can be shown by an examination of the data obtained by Ramsay and Steele.[6]

These investigators determined the vapor density for a number of substances at a series of pressures ranging between 40 and 755 mm of mercury. The molecular weights obtained from their data by means of a linear extrapolation through the points at one and at one-half atmosphere are close to the true molecular weights, although not, in general, as close as are the values obtained by extrapolating the actual curves through their observed points. The discrepancies are, however, small in both cases, and are within the experimental errors of the technic of the present method. These comparisons are shown in Table 1.

[6] See footnote 4, p. 576.

TABLE 1.—*Comparison of molecular weights obtained by different methods from Ramsay and Steele's measurements* [1]

	Molecular weight		Per cent difference (*b*)-(*a*)	Molecular weight by linear extrapolation (*c*)	Per cent difference (*c*)-(*a*)	Molecular weight from gas laws (*d*)	Per cent difference (*d*)-(*a*)
	True (*a*)	Bygraph. extrapolation (*b*)					
Diethyl ether	74.077	73.95	−0.17	73.75	−0.42	74.84 at p=605 mm	+1.04
Methyl alcohol	32.031	32.03	−.003	31.97	−.11	32.264 at p = 517 mm	+.73
Benzene	78.046	78.15	+.13	77.94	−.15	79.71 at p = 755 mm	+2.13
n-Octane	114.14	114.57	+.38	114.48	+.30	118.84 at p = 573 mm	+3.33
n-Hexane	86.108	86.03	−.09	85.85	−.30	88.05 at p = 607 mm	+3.41
Diisobutyl	114.14	114.19	+.03	113.84	−.26	118.59 at p = 565 mm	+3.90
Toluene	92.062	92.46	+.43	91.89	−.19	93.95 at p = 671 mm	+3.15

[1] Ramsay and Steele, Z. phys. Chem., 44, p. 348; 1903.

The largest differences resulting from the use of either method of extrapolation are approximately 3 parts in 1,000, while those resulting from the direct application of the ideal gas laws are of the order of 1 to 4 parts in 100.

IV. RESULTS WITH HYDROCARBONS

In this investigation the molecular weight has been determined for benzene,[7] synthetic *n*-hexane,[8] *n*-hexane from petroleum [9] and naphthalene.[10]

Three sets of results are given for the *n*-hexane from petroleum as it was known to contain carbon dioxide, water, and other impurities. For the first measurement no purification of the sample was made. For the second measurement the carbon dioxide was removed by heating the substance to the boiling point, under reflux, and bubbling air through the liquid. For the third measurement the hexane was distilled from metallic sodium to remove the water.

The correction for the liquid volume of the sample was made. The additional small correction for the vapor space left in the bulb was found to be of approximately the same size as and of opposite sign to the one for the dissolved air in the sample (0.08 per cent for benzene). These were considered to cancel each other. The weights were corrected ad vacuum.

Table 2 shows the values for the calculated molecular weight of benzene and their differences from the true molecular weight. The value found for the coefficient A for benzene is 0.0244. The value, calculated from the critical-point constants, is 0.0224.

Tables 3 and 4 give the experimental molecular weights for naphthalene, synthetic *n*-hexane, and the *n*-hexane from petroleum. The value found for the coefficient A for naphthalene is 0.00823. Since naphthalene is subject to decomposition, its critical temperature and pressure are unknown.

[7] Benzene (C. P. grade) was treated with concentrated H_2SO_4 and subsequently washed with dil. NaOH and water. It was recrystallized and then distilled from metallic sodium. It had a freezing range of less than 0.2° C.

[8] Obtained from Eastman Kodak Co. Refractive index, $n_D^{20} = 1.376$.

[9] Bruun and Hicks-Bruun, B. S. Jour. Research, 5, October, 1930.

[10] Naphthalene (C. P. grade) sublimed and recrystallized. Freezing range less than 0.2° C.

TABLE 2.—*Experimental data for molecular weight of C_6H_6*

Molecular weight calculated from measurements at 1 atmosphere	Per cent difference from true value 78.046	Molecular weight calculated from measurements at 0.5 atmosphere	Per cent difference from true value 78.046
78.06	+0.02	77.93	−0.15
78.13	+ .10	78.07	+ .03
78.01	+ .05	77.95	− .12
77.90	− .19	77.99	− .08
77.90	− .19	77.96	− .11
78.00	− .06	78.13	+ .10
78.08	+ .05	77.97	− .09
77.99	− .08	78.07	+ .03
Mean = 78.01	Average deviation, 0.10 per cent. Maximum deviation, 0.19 per cent.	Mean = 78.01	Average deviation, 0.09 per cent. Maximum deviation, 0.15 per cent.

TABLE 3.—*Experimental data for molecular weight of $C_{10}H_8$ and synthetic C_6H_{14}*

Experimental molecular weight for $C_{10}H_8$	Per cent difference from true value 128.06	Experimental molecular weight for C_6H_{14} synthetic	Per cent difference from true value 86.108
128.02	0.04	86.26	+0.17
128.00	.06	86.32	.24
128.00	.06	86.18	.08
128.00	.06	86.15	.05
Mean=128.00	Average and maximum deviation, 0.06 per cent	Mean=86.23	Average deviation, 0.14 per cent; maximum deviation, 0.24 per cent

TABLE 4.—*Experimental data for "n-hexane from petroleum"*

[Purity, about 92 mole per cent]

[Showing the effects of dissolved moisture and carbon dioxide]

Experimental molecular weight before removing CO_2 and H_2O	Experimental molecular weight after removing CO_2	Experimental molecular weight after removing CO_2 and H_2O
84.61	85.42	85.58
84.49	85.47	85.61
Mean=84.55	Mean=85.45	Mean=85.60
	Increase=1.07 per cent	Increase=0.19 per cent

The mean precision which this apparatus has been found to give is approximately 3 parts in 1,000. The accuracy of the molecular weight obtained is about 2 parts in 1,000. The maximum deviations and the difference between the mean experimental value and the true molecular weight of benzene are shown in Figure 3 by lines drawn

through a plot which has been made of the 16 experimental values obtained. The greater discrepancy (6 parts in 1,000) in the case of the final results for the *n*-hexane from petroleum is attributable to impurities which were known to be present.

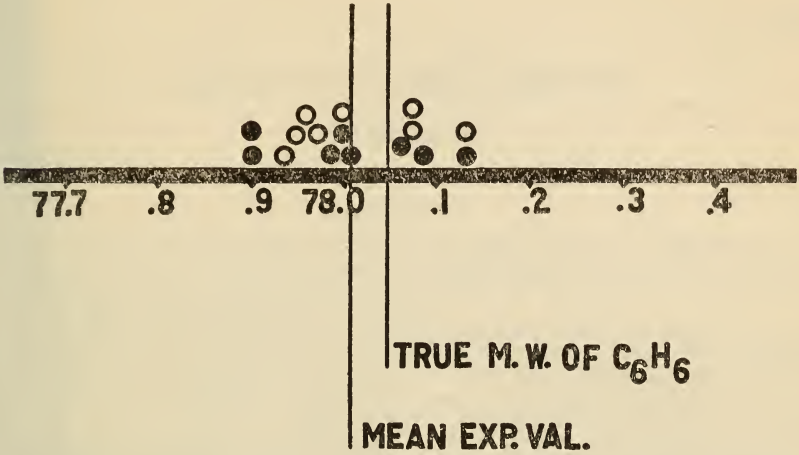

FIGURE 3.—*Plot of experimental values for the molecular weight of benzene*
The white-centered circles represent the values obtained from measurements at 0.5 atmosphere.

This research was conducted under the direction of E. W. Washburn to whom the writer is greatly indebted for guidance throughout this work.

WASHINGTON, April 25. 1930.